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Structural investigation of hydrous sodium borosilicate glasses

U. Bauer^{a,b}, H. Behrens^{a,b,*}, S. Reinsch^c, E.I. Morin^d, J.F. Stebbins^e^a Leibniz Universität Hannover, Institute of Mineralogy, Callinstr. 3, 30167 Hannover, Germany^b ZFM, – Center for Solid State Chemistry and New Materials, Leibniz Universität Hannover, Germany^c Federal Institute for Materials Research and Testing, BAM, 12489 Berlin, Germany^d Stanford University, Department of Chemistry, Stanford, CA 94305, USA^e Stanford University, Department of Geological Sciences, Stanford, CA 94305, USA

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ABSTRACT

The structural properties of a borosilicate glass with nominal 16 mol% Na₂O, 10 mol% B₂O₃ and 74 mol% SiO₂ and water contents between 0 and 8 wt% H₂O (0–22 mol% H₂O) were investigated with IR, Raman and ¹¹B MAS NMR spectroscopy. In addition to the pronounced OH stretching vibration band of weakly H-bonded species at 3580 cm⁻¹ the MIR spectra show a triplet at 2900, 2350 and 1750 cm⁻¹, similar as observed in water-bearing silicate glasses. These bands are assigned to OH groups and water molecules which are strongly H-bonded, to non-bridging oxygen. Water species contents determined from absorption bands in the NIR at 5200 cm⁻¹ (molecular H₂O), 4700 cm⁻¹ (B–OH), and 4500 cm⁻¹ (Si–OH) indicate that hydroxyl groups dominate up to ~6 wt% total H₂O. Based on the absorption coefficients known from literature for silicate and borate glasses the B–OH/Si–OH ratio is estimated to be ≈0.8.

As indicated by density, Raman and NMR data the incorporation of water has strong structural impacts in particular at low water contents up to 3 wt% H₂O. While the nominally dry glasses still contain a significant fraction (12%) of three-fold coordinated boron, almost all boron is four-fold coordinated in hydrous glasses.

The increase of band components in the Raman spectra near 900 cm⁻¹ relative to the region > 1050 cm⁻¹ gives evidence for depolymerization of the network upon hydration. Fitting of the spectra with Gaussians implies that silica tetrahedra with two non-bridging oxygen (Q²) are preferentially formed by reaction with water on expense of tetrahedra linked to four tetrahedra (Q⁴).

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1. Introduction

Borosilicate glasses were intensively investigated in the past because of their wide range of technical glass applications as e.g. optical glasses or as container material of nuclear waste. Special features of such glasses are e.g. high chemical durability and thermal-shock resistivity.

With the addition of alkalis or alkaline-earth oxides to boron containing glasses, boron initially present as trigonal planar groups (BO₃) is converted to four-fold coordinated boron (BO₄) species, with partial charges on bridging oxygens compensated by the added cations. At high alkali or alkaline-earth contents, the excess oxygens act as non-bridging oxygens (NBO) and result in a depolymerization of the network and the conversion from BO₄ to BO₃. Temperature and pressure also affect the boron coordination and hence causes changes e.g. in density, thermal expansion and mechanical properties of the glass [1–12].

Glasses of technical relevance typically contain much less than one weight percent H₂O (e.g. <0.1 wt% H₂O in silicate and borosilicate < 1 wt% H₂O in borate and phosphate glasses). High water contents of several weight percent are common in natural systems such as volcanic glasses, but are usually of minor importance for industrial glass production. However, such high water contents may become of interest for water-related fatigue of glasses since water easily can be absorbed and accumulated for instance at crack tips or near the glass surface and lead to corrosion.

The influence of water on glass properties in boron-bearing glasses has been much less investigated compared studies of silicate and aluminosilicate glasses. Water and alkali oxides can both depolymerize the melt structure and thus reduce the viscosity of the melt [13,14], whereby the effect of water is stronger compared to alkalis, e.g. [15]. It is known that water in glasses is present as two main species: as molecular water and as water dissolved in the form of OH groups [14,15,16,17]. The fractions of the two different water species present in silicate and aluminosilicate glasses, are, however, very different from those in boron-rich glasses. In silicate glasses and aluminosilicate glasses with less alumina than silica OH groups predominate only up to moderate water contents (<4 wt% H₂O) [18–21]. On the other hand, in potassium

* Corresponding author at: Leibniz Universität Hannover, Institute of Mineralogy, Callinstr. 3, 30167 Hannover, Germany.

E-mail address: h.behrens@mineralogie.uni-hannover.de (H. Behrens).

aluminosilicate glasses with more alumina than silica H_2O molecules are the minor species even at 7 wt% H_2O because of the strong aluminum avoidance and the strong tendency for Al–O–Al linkages to hydrolyze in such glasses [22]. An increasing abundance of OH groups with increasing boron content was observed in sodium aluminoborosilicate glasses [23] and OH groups are predominantly present in borate glasses even for water contents ≥ 8 wt% H_2O [24], reflecting a trend of increasingly stabilized OH groups with rising boron content.

In soda lime borate glasses it was recently found that the effect of water on the stabilization of boron in tetrahedral coordination is ten times lower compared to that of alkalis, probably because protons are much more localized compared to alkalis [24]. For aluminoborosilicate glasses a slightly larger influence of water on B speciation was discovered [23].

In this study ^{11}B MAS NMR, Raman, MIR and NIR spectroscopy are applied to improve the knowledge about the role of water in the borosilicate glass network. Kinetic aspects of these glasses obtained from measurements of the glass transition temperature, viscosity and internal friction are discussed in a forthcoming paper.

2. Experimental and analytical methods

2.1. Starting materials

For the synthesis of borosilicate glass containing nominal 16 mol% Na_2O , 10 mol% B_2O_3 and 74 mol% SiO_2 powder mixtures of Na_2CO_3 , B_2O_3 and SiO_2 were melted in a 2.4 l platinum crucible at 1603 K for 3.5 h in an induction furnace. During the last 40 min at 1603 K the melt was stirred 20 min in the lower part and 20 min in the upper part of the platinum crucible to facilitate homogenization. Subsequently the temperature was raised to 1673 K. After 1 h the melt was poured into a preheated graphitized steel mold. The obtained glass ingots were transferred into a furnace preheated at 893 K and subsequently cooled in the switched-off furnace during the night for stress relaxation. Unfortunately the exact cooling rate of the ambient pressure glass was not measured. However, we estimate a cooling rate of <10 K/min for the range of glass transition and type of furnace. The composition of the NBS start glass was analyzed by inductively coupled plasma-optic emission spectrometry (ICP-OES, 715-ES VARIAN). ~ 50 mg sample material were dissolved by microwave digestion using 4 ml 85% H_3PO_4 , 3 ml 65% HNO_3 and 1 ml 40% HF. The specified contents are based on three individual analyses (16.00 ± 0.21 mol% Na_2O , 9.97 ± 0.11 mol% B_2O_3 and 74.03 ± 0.30 mol% SiO_2). The NBS start glass was crushed with a steel mortar to powder which was subsequently used for the synthesis of hydrous and compressed glasses.

2.2. Hydrous and compressed glasses

For syntheses of hydrous glasses, glass powder and distilled water were filled stepwise in turn in a platinum capsule (diameter: 6 mm, length: 25–30 mm) to facilitate homogeneous distribution of water in the glass. To produce anhydrous compressed glasses only the starting glass powder was loaded into the platinum capsules. By subsequent compaction of the material in the capsule using a steel piston a cylindrical shape of glass bodies was achieved. After sealing with a PUK welding device (PUK3 Professional Plus, Lampert GmbH) the capsules were checked for possible leakage by measuring the weight loss after storage in a drying furnace at 373 K.

Syntheses were performed in an internally heated pressure vessel (IHPV) at 500 MPa and 1423 K for 14–20 h using argon as pressure medium. In each run 2–3 capsules were placed in the hot spot zone of the sample holder between the two furnace-controlling K-type thermocouples (Ni–CrNi). The temperature of the samples was monitored by a third thermocouple located in the middle of the hot spot zone. The maximum variation in temperature during the synthesis was ± 10 K, and pressure accuracy is within ± 50 bars. In order to preserve pressure

induced structural changes and to avoid water loss of the glasses, samples were isobarically quenched using an automatic pressure controller (normal quench, NQ) when switching off the furnace. This leads to a cooling rate in the regime of T_g of ~ 8 K/s for NBS0–500 MPa, NBS0.5 and NBS1, ~ 6 K/s for NBS3 and ~ 3.5 K/s for NBS5. The sample containing 8 wt% H_2O was quenched much faster (~ 200 K/s) through the range of glass transition using a rapid quench (RQ) sample holder since the sample was partially crystallized in a first trial when using the NQ procedure. A detailed description of the RQ method for IHPV is given in Berndt et al [25].

All glass cylinders were clear and no crystals or bubbles were observed after high pressure synthesis. This implies that synthesis conditions were volatile-undersaturated, which means that H_2O solubility in the borosilicate glass is significantly above 8 wt% at 1423 K and 500 MPa. For IR and KFT measurements glass pieces were cut from each end of the glass body to test for homogeneous distribution of water (Table 1). Exposure of glasses to water was avoided and oil was used for sawing and polishing samples, e.g. for preparation of thin sections for spectroscopy. In the following, the number in the sample name refers to the nominal water content and roman numerals are used to distinguish glass pieces cut from both ends of the glass body.

2.3. Analysis of water content and speciation

The total water content $c_{\text{H}_2\text{O,t}}$ of the glasses was determined by pyrolysis and subsequent Karl–Fischer Titration (KFT). The analysis procedure for the borosilicate glasses was the same as reported in Bauer et al. 2015 [24]. A detailed description of the method is given in [19,26–29].

IR spectra were collected on sections polished on both sides using a Fourier Transform Infrared (FTIR) spectrometer (Bruker IFS88) coupled with an IR microscope (Bruker IR scope II) equipped with a mercury-cadmium-tellurium (MCT) detector. Absorption spectra in the mid-infrared (MIR) were recorded to investigate fundamental OH stretching vibrations and to determine $c_{\text{H}_2\text{O,t}}$ of nominal dry glasses. A KBr beam splitter and a global light source were used, and spectra were recorded in the range of 600 to 6000 cm^{-1} with a spectral resolution of 2 cm^{-1} . 50 scans for sample and background (air) measurements were accumulated. A slit aperture between the objective and the detector was used to limit the analyzed sample volume. In the focus plane, the area selected by the slit was typically $(100 \times 100) \mu\text{m}^2$.

To determine different water species contents of H_2O molecules ($c_{\text{H}_2\text{O,mol}}$) and water dissolved in form of OH groups (c_{OH}) near-infrared (NIR) spectra were collected using a tungsten light source and a CaF_2 beam splitter in combination with the MCT detector. Spectra were measured in the range of 2000–11,000 cm^{-1} with a spectral resolution of 4 cm^{-1} and 100 scans were accumulated for each spectrum. As in the case of measurements in MIR an area of $(100 \times 100) \mu\text{m}^2$ in the focus plane was selected. At least three spectra for each sample were measured to check the reproducibility of the collected spectra and the homogeneity of water distribution in the glass. Additional samples produced for dynamic mechanical analysis (DMA) are also included in our spectroscopy study (indicated by DMA in Table 1). Here, NIR spectra were collected on bulk samples using a 2 mm aperture and an Indium SB D 413 detector. An aperture plate of 2 mm in diameter was chosen to limit the analyzed sample volume. The spectral resolution in the NIR was 2 cm^{-1} and 100 scans were accumulated for background and sample measurements. The thickness of the glass sections and bars were measured using a digital micrometer (Mitutoyo) with a precision of $\pm 2 \mu\text{m}$. The average thickness of each sample is listed in Tables 1 and 2.

2.4. DTA and density measurements

The glass transition temperature, T_g , was measured by differential thermal analysis (DTA) in air using glass pieces or powdered glass of

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